



Thermal stability and dehydration of armstrongite, a microporous zirconium silicate



E. Schingaro^a, M. Lacalamita^{b,*}, E. Mesto^a, G. Della Ventura^{c,d}

^a Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "Aldo Moro", via E. Orabona 4, I-70125, Bari, Italy

^b Dipartimento di Scienze della Terra, Università di Pisa, via S. Maria 53, I-56100, Pisa, Italy

^c Dipartimento di Scienze, Università di Roma Tre, Largo S. Leonardo Murialdo 1, I-00146, Roma, Italy

^d INFN-Laboratori Nazionali di Frascati, Via E. Fermi 40, I-00044, Frascati, Roma, Italy

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ABSTRACT

The dehydration of armstrongite from Khan Bogdo (Mongolia) was investigated by combining thermal analysis, *in situ* HT X-ray powder diffraction (XRPD) and Fourier Transform InfraRed (FTIR) spectroscopy. The process starts at $\sim 380^\circ\text{C}$ and is completed within few tenths of degrees. It involves a mass loss of 6.1 wt% and a cell volume decrease of 7%. Armstrongite at RT has $C2/m$ symmetry with (in \AA) $a = 14.010$ (2), $b = 14.115$ (1), $c = 7.838$ (1), $\beta = 109.387$ (3)°, $V = 1462.2$ (2) \AA^3 . XRPD data in the T-range $370\text{--}400^\circ\text{C}$ show a significant contraction of the cell volume without any symmetry change. At 400°C the dehydrated phase has cell dimensions (in \AA): $a = 13.425$ (2), $b = 13.752$ (1), $c = 7.818$ (1), $\beta = 110.246$ (3)°, $V = 1354.2$ (2) \AA^3 . The patterns collected in the T-range from 800 to 30°C show that armstrongite rehydrates quickly at $T \sim 320^\circ\text{C}$; unit cell parameters and volume refined at the end of the heating/cooling cycle point to a complete reversibility of the dehydration process. Fast rehydration upon cooling is also evident in the FTIR spectra; a complete recovery of the OH-stretching and bending signals is observed at $T \sim 280\text{--}300^\circ\text{C}$. Notably, this process can be monitored on single-crystals, while powders embedded in KBr pellets do not recover the structural water content. The thermal expansion of armstrongite is more pronounced along the b axis, with α_a : α_b : $\alpha_c = 1.09 \times 10^{-6}$: 1.69×10^{-5} : 7.61×10^{-7} at 90°C and 7.73×10^{-6} : 8.94×10^{-6} : 5.85×10^{-6} at 800°C .

1. Introduction

Armstrongite, $\text{CaZr}[\text{Si}_6\text{O}_{15}]\cdot 2\text{H}_2\text{O}$, is a microporous Zr-silicate with a crystal structure based on a heteropolyhedral framework, consisting of SiO_4 tetrahedra and ZrO_6 octahedra, giving rise to cavities occupied by Ca-exchangeable cations. The crystal structure was studied by a number of authors [1–4] but only recently Mesto et al. [5] were successful in defining some debated structural details, such as the space group and the content and location of water molecules. These authors carried out a single crystal structure refinement on armstrongite from Khan Bogdo massif (Gobi, Mongolia) showing that the mineral crystallizes in the $C2/m$ space group with lattice parameters: $a = 14.0178$ (7) \AA , $b = 14.1289$ (6) \AA , $c = 7.8366$ (3) \AA , $\beta = 109.436$ (3)°, $V = 1463.6$ (1) \AA^3 , $Z = 4$. In the structural model, silicate radicals, in the form of $[\text{Si}_6\text{O}_{15}]^{6-}$ sheets, are connected by vertices to ZrO_6 octahedra. The latter are linked via edges to seven-fold coordinated $\text{CaO}_5(\text{H}_2\text{O})_2$ polyhedra to form columns running parallel to the crystallographic b axis. The occurrence of only two water groups per formula unit was inferred after the XRD refinement and supported by

infrared analysis. The final crystal chemical formula, based on X-ray and EMP data was $(\text{Ca}_{0.96}\text{Ce}_{0.01}\text{Yb}_{0.01})\text{Zr}_{0.99}\text{Si}_6\text{O}_{14.97} \cdot 2.02\text{H}_2\text{O}$. The calculated framework density of the mineral (21.86 per 1000\AA^3) allowed it to be definitely classified as a zeolite-like phase.

In the last years increasing attention has been addressed to zeolite-like materials because of their potential application in the fields of catalysis, ion exchange and sorption [e.g.6,7] and study on natural materials (minerals) are of interest prior to the production of synthetic counterparts [8].

On the other hand, most of the chemical and physical processes involving porous materials are indeed affected by structural water molecules. For example, the efficiency of the ion exchange process may depend on the hydration degree of the extraframework cations [9]. In particular, the water molecules play a role in the distribution and interaction of exchangeable cations with the structural framework, especially in relation to temperature changes [10].

The present study aims at characterizing the thermal behaviour of armstrongite that, to the best of our knowledge, has never been explored so far. To this purpose, we combine thermal techniques

* Corresponding author.

E-mail address: maria.lacalamita@dst.unipi.it (M. Lacalamita).

(Differential Thermal Analysis, DTA, Thermo Gravimetry, TG and Differential Thermo Gravimetry, DTG), *in situ* High Temperature X-Ray Powder Diffraction (HTXRPD) and *in situ* High Temperature Fourier Transform InfraRed spectroscopy (HT-FTIR) measurements, both from powders and single-crystal, on the same armstrongite specimen studied by Mesto et al. [5].

2. Experimental

The armstrongite specimen studied here has been separated from the same rock sample (608/19a) studied by Vladykin [11] and Vladykin and Kovalenko [12]. The geological setting is reviewed elsewhere [5].

Thermogravimetric analysis was carried out using a DTA-TG SEIKO 6300. A Pt crucible was filled with 11.5 mg of powdered armstrongite and heated at a rate of 10 °C/min, from room temperature up to 1000 °C.

High-temperature X-ray powder diffraction data were collected in air using a Panalytical Empyrean X-ray diffractometer with Bragg-Brentano geometry, large beta filter-Nickel detector (PIXcel3D) and CuK α radiation, operating at 40 kV/40 mA. The instrument was equipped with an Anton Paar HTK 1200 N high-temperature chamber. The powder was deposited on a corundum sample holder. The X-ray data were collected in the 2 θ range 10–65° (step size 0.0263°, step time 22.440s) from 30° to 800 °C and back. The temperature step on heating/cooling rate was 10 °C/min and the equilibration time at every 10 °C temperature step was 10 min. Diffraction patterns were processed using the PANalytical B.V. software HIGHscore Plus version 3.0e. Structure refinements were carried out in the C2/m space group by the Rietveld method as implemented in GSASII [13], starting from the structure model of Mesto et al. [5]. The scale factor, lattice parameters and atomic coordinates were refined while the isotropic-displacement parameters were kept fixed. The zero shift was refined at each step; the background was modelled using a Chebychev polynomial approximation of 15 th order. The peak profile was described by a pseudo-Voigt. The orientation of the principal axes of the thermal-expansion tensor with respect to the crystallographic axes was determined using the TEV program [14].

The *in situ* dehydration of armstrongite was monitored via FTIR spectroscopy both on powders and single-crystals. In the former case, ~0.5 mg of sample were embedded in 150 mg of KBr and pressed; data were collected with a Nicolet iS50 FTIR spectrometer equipped with a DTGS detector and a KBr beamsplitter; the nominal resolution was 4 cm⁻¹ and 64 scans were averaged for both sample and background. In the latter case a very thin crystal fragment was used; data were acquired on a Bruker Hyperion 3000 IR microscope, equipped with a KBr beamsplitter and a N₂-cooled MCT detector, with a beam diameter of 40 μ m. Heating experiments were conducted using a Linkam T600 heating/freezing stage, fitted in the FTIR microscope (single-crystal); the cell is tightly closed to avoid any contact with the external atmosphere. Experiments with the powder pellet were done using a Specac high T/P call fitted in the optical bench. The heating ramps from 30 to 550 °C were done with a 10°/min T rate and spectra were collected every 20 or 10 °C, depending on the T segment, immediately after reaching the target T; reverse experiments were done by collecting spectra every 20 or 50 °C.

3. Results

3.1. Thermogravimetric analysis

The TG-DTA-DTG curves collected on the studied armstrongite are displayed in Fig. 1. The sample exhibits two steps of thermal degradation associated with desorption of water. The first step occurs up to ~100 °C, with a mass loss of ~0.5 wt%, and corresponds to the release of adsorbed water. The second step is observed in the range 100–400 °C and shows a significant mass loss (~6.1 wt%) of the

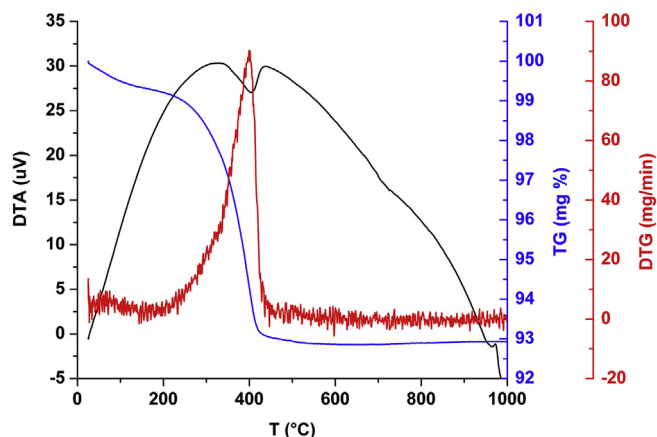


Fig. 1. TG (blue line), DTG (red line) and DTA (green line) curves of armstrongite measured in air. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

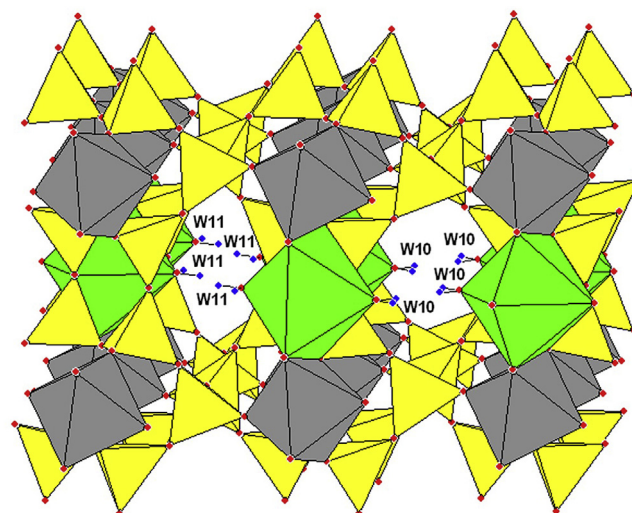


Fig. 2. Armstrongite heteropolyhedral framework, modified after [5] as seen slightly off the c axis. W10 and W11 are water molecules coordinated by the Ca polyhedron (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

sample. It is associated to the release of the water molecules (W10 and W11) coordinated by the Ca extraframework cations (Fig. 2). This process is clearly visible in the DTA plot as a strong endothermic peak. According to the DTG curve, the weight-loss has a very steep increase in the 300–400 °C range and occurs abruptly at T ~ 400 °C. The DTA curve shows a weak endothermic peak at 700 °C and an exothermic peak at 980 °C, whereas no changes are observed in the TG-DTG curves at these temperatures. These effects may be associated to structural modifications induced by heating.

3.2. *In situ* HT-XRPD

Rietveld refinements were performed for all patterns and provided agreement factors, R_{wp} , in the range from 6.67 to 8.00%. Details are given in Table S1 (submitted as supplementary material).

The room temperature XRPD pattern of the studied armstrongite matches exactly the expected pattern from the PDF database (01-074-2684 PDF number). In Fig. S3 the Rietveld refinement of the RT data obtained using the structure model from Mesto et al. [5] is shown. Unit cell parameters very close to those derived from single crystal structure refinement were obtained (see Table S1). Peaks of quartz impurities are observed in the XRPD patterns, amounting to less than 4%, as

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